Simultaneous catalytic reduction of NO and N_2O using Fe-MFI prepared by solid-state ion exchange

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Received 20 November 1997; accepted 3 February 1998

Solid-state ion exchange in the presence of air has been used to prepare Fe-MFI catalysts that exhibit activities comparable to preparations obtained under anaerobic conditions. Preliminary results obtained during the simultaneous catalytic reduction of NO and N_2O with propane in the temperature range from 473 to 773 K show that Fe-MFI might be of interest for the treatment of exhaust gases containing NO_x and nitrous oxide. Undesirable CO formed in a side-reaction can be oxidized to CO_2 by promotion of Fe-MFI with small amounts of Pt.

Keywords: nitrous oxide, nitric oxide, reduction, propane, Fe-MFI, platinum

1. Introduction

The development of catalysts for the removal of nitrogen oxides in the presence of excess oxygen still remains a major challenge. Since it is generally accepted that the long-term stability of Cu-MFI in the presence of water vapour and sulphur dioxide is not sufficient for technical applications [1], research effort is shifting to other catalyst systems. While the use of Fe-MFI for decomposition of nitrous oxide has been described in a few papers [2–4], interest in this material is strongly increasing since it has been described that highly active catalysts for the hydrocarbon reduction of N_2O [5] and NO [6–8] can be obtained if special preparation methods are employed. It has been shown that these catalysts are stable under hydrothermal conditions and resistant to exposure to sulphur dioxide [6,7]. However, all active Fe-MFI preparations described so far have been obtained under anaerobic conditions, because otherwise, as has been pointed out by Delgass et al. [9], Fe^{2+} cations are oxidized in aqueous medium to precipitate iron hydroxide. While Pophal et al. [5] used iron sulphate for ion exchange under nitrogen atmosphere, Feng and Hall [7] employed iron oxalate in a special apparatus allowing for the separation of salt and zeolite powder. Chen and Sachtler [8] used the sublimation of a volatile iron component into the acid form of MFI under inert atmosphere. The importance of these special measures during preparation of Fe-MFI is demonstrated by results obtained by Joyner and Stockenhuber [10] and by Kapteijn et al. [4]. These authors used aqueous ion-exchange procedures in the presence of air, and in both cases, catalysts with relatively low activity during reactions of nitrogen oxides were obtained.

An alternative method for the introduction of cations into zeolites, the so-called solid-state ion exchange, has been proposed by Karge and Beyer [11,12]. To our knowledge, only two publications deal with the use of this method for the preparation of Fe-MFI. While Varga et al. [13] did not carry out catalytic tests, Dandl [14] used Fe-MFI obtained by solid-state ion exchange in the absence of oxygen for the decomposition of N_2O. The aim of the present paper is to demonstrate that Fe-MFI catalysts with activities comparable to the anaerobic preparations can be obtained by solid-state ion exchange even in the presence of air. The catalysts are suitable for the simultaneous catalytic reduction of NO and N_2O by propane.

2. Experimental

The iron-exchanged MFI catalysts were prepared by solid-state ion exchange of commercial MFI zeolite with $Si/Al = 11.4$ [15]. The sodium (SN 27) and ammonium (SM 27) forms were used as received, while H-MFI was prepared by calcination of NH_4-MFI at 773 K for 4 h. 3 g of zeolite were mechanically mixed with $FeCl_2 \cdot 4H_2O$ (adjusted to a molar ratio of $Fe/Al = 0.75$) for 1 h in a ball mill. The mixture was heated to 823 K within 3 h and kept at this temperature for 6 h in air. The product was cooled to ambient temperature, washed thoroughly in deionized water and dried at 383 K overnight. A Pt/$FeNH_4$-MFI sample was prepared by wet impregnation of 3 g of calcined $FeNH_4$-MFI in 500 ml of a dilute $Pt(NH_3)_4(NO_3)_2$ solution for 24 h. Assuming complete platinum uptake, the Pt content of the catalyst is 0.01 wt%. Finally, the zeolite powder was pressed to tablets, crushed and sieved to obtain a fraction of 315–500 μm.

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The catalysts (0.40 g) were placed in a quartz tube reactor which was heated electrically. The temperature in the catalyst bed was measured using a thermocouple. The gases N_2O, NO, O_2, C_3H_8 and He were added via thermal mass flow controllers (Brooks, 5850). The exit concentrations were monitored by means of a magnetic oxygen analyzer (Hartmann und Braun, Magnos 6G), nondispersive infrared analyzers for N_2O, NO, CO, CO_2 (Rosemount, Binos 4), and an UV photometer for NO_2 (Rosemount, Binos 5). The conversion of propane was calculated from the amounts of CO and CO_2 formed. The catalysts were pretreated in flowing helium (500 cm^3/min, NTP) at 773 K for 1 h. The measurements were then carried out in the temperature range from 473 to 773 K, typically using a gas mixture of 1000 ppm N_2O, 800 ppm NO, 4% O_2 and 1000 ppm C_3H_8 in helium. A total flow rate of 400 cm^3/min (NTP) was employed, i.e., the gas hourly space velocity (GHSV) based on a density of 0.5 g/cm^3 for the catalyst bed amounted to 30,000 h^{-1}.

3. Results and discussion

Elemental analysis of the iron-exchanged zeolites was carried out by using ICP. The results summarized in table 1 reveal that no iron was lost during calcination. XRD analysis of the different Fe-MFI samples showed the absence of crystalline iron chloride, whereas traces of Fe_2O_3 (hematite) could be observed in all cases. In a preliminary series of experiments, the reduction of nitrous oxide with propane was carried out over Fe-MFI catalysts obtained from the three different starting materials (cf. figure 1). The poor catalytic activity of FeNa-MFI is most probably caused by a low content of ion-exchanged iron ($n_{\mathrm{Na}}/n_{\mathrm{Al}} = 0.91$) in this sample. An explanation for the significant activity differences between $FeNH_4$-MFI and FeH-MFI, which are observed despite a similar iron content within about 10% (cf. table 1), can only be given after further characterization of these catalysts. However, it is evident that the best preparation based on NH_4-MFI exhibits high catalytic activity for the hydrocarbon reduction of N_2O that is comparable to the results obtained by Pophal et al. [5] using propene as reducing agent.

Table 1
Chemical composition of iron-exchanged zeolites.

	FeNa-MFI	FeH-MFI	$FeNH_4$-MFI
$n_{\mathrm{Si}}/n_{\mathrm{Al}}$	11.7	11.3	11.4
$n_{\mathrm{Na}}/n_{\mathrm{Al}}$	0.91	0.006	0.006
$n_{\mathrm{Fe}}/n_{\mathrm{Al}}$	0.775	0.757	0.842

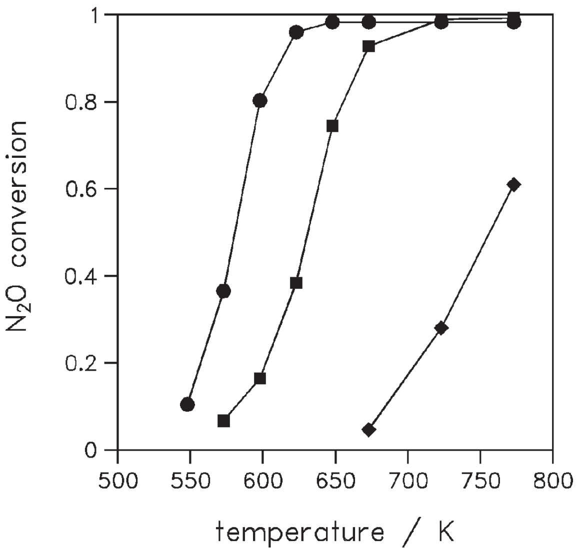

Figure 1. N_2O conversion as a function of temperature. (●) $FeNH_4$-MFI, (■) FeH-MFI, (◆) FeNa-MFI. Reactant feed: 1000 ppm N_2O, 1000 ppm C_3H_8 and 4% O_2 in He at GHSV 30,000 h^{-1}.

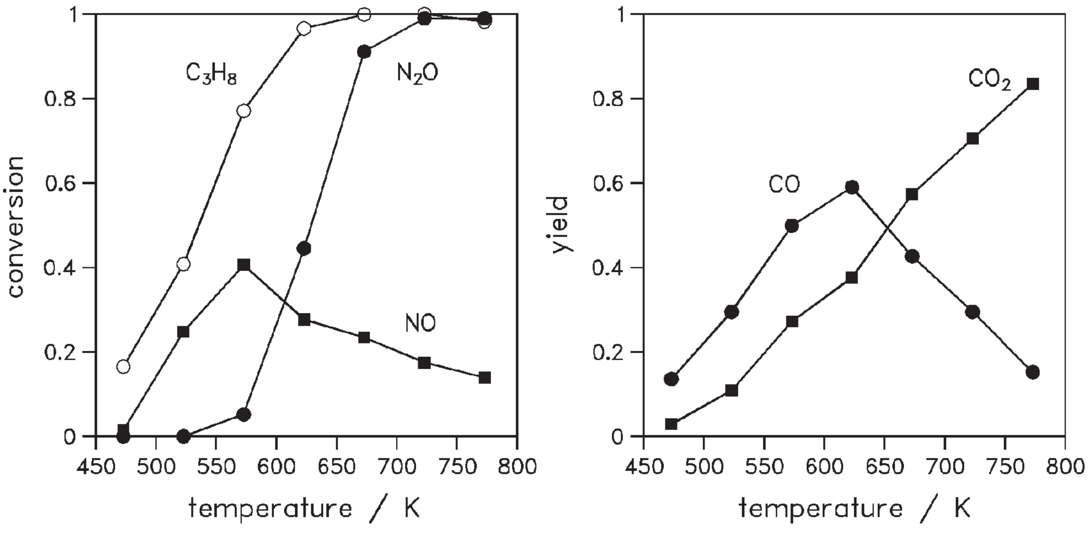

Figure 2. Propane conversion (open symbols), N_2O and NO conversion to nitrogen over $FeNH_4$-MFI as a function of temperature (left-hand side). CO and CO_2 yield as a function of temperature (right-hand side). Reactant feed: 1000 ppm N_2O, 800 ppm NO, 1000 ppm C_3H_8 and 4% O_2 in He at GHSV 30,000 h^{-1}.

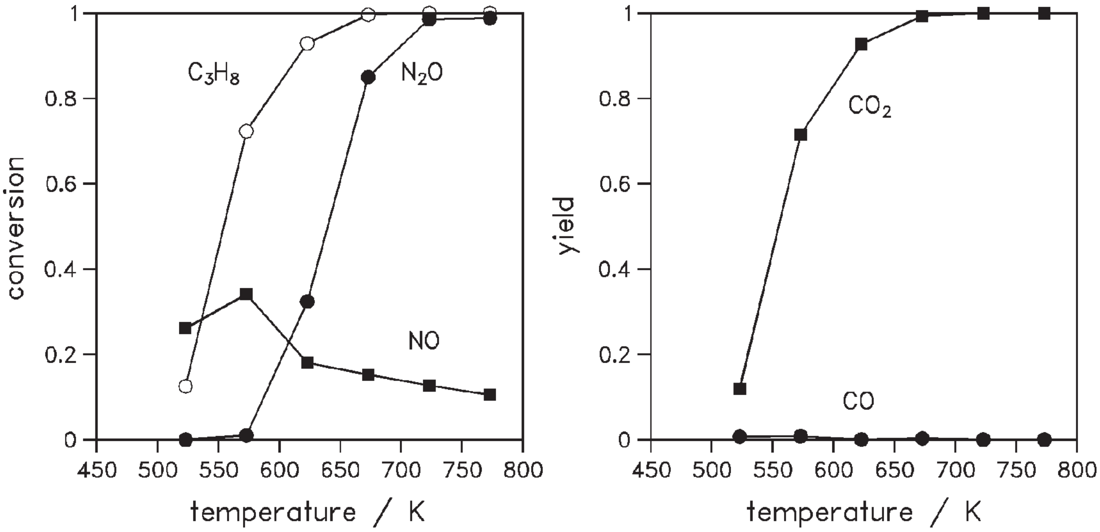

Figure 3. Propane conversion (open symbols), N_2O, NO conversion to nitrogen (left-hand side), CO and CO_2 yield (right-hand side) over Pt/FeNH_4-MFI as a function of temperature. Reaction conditions as per figure 2.

The catalyst prepared from the ammonium form of MFI was then subjected to the simultaneous catalytic removal of NO and N_2O. Figure 2 shows the conversion of the nitrogen oxides to nitrogen, the hydrocarbon conversion as well as the CO and CO_2 yield as a function of temperature. It can be seen that the nitrous oxide conversion is lower than during the experiment without added NO (figure 1), but N_2O is still completely removed at temperatures above 700 K. For NO, a maximum conversion of 40% at 573 K is observed under the reaction conditions used. Propane is completely converted above 600 K, but it has to be noted that carbon monoxide is formed as a byproduct. Similar observations were made by Chen and Sachtler [8] in the reduction of NO with isobutane over Fe-MFI.

The results obtained with the Pt/FeNH_4-MFI catalyst (figure 3) reveal that undesirable carbon monoxide formed during the reduction of nitrogen oxides with hydrocarbons can be easily oxidized to carbon dioxide by adding small amounts of Pt to Fe-MFI, while NO and N_2O conversions remain slightly lower than using FeNH_4-MFI (figure 2).

In conclusion, we have shown that solid-state ion exchange in the presence of air, a method that can be easily transferred to the large-scale manufacture of Fe-MFI, allows for the preparation of catalysts with activities that have been so far obtained only under anaerobic conditions. Fe-MFI offers the ability to reduce both NO and N_2O emissions in one step, and the achievable conversions appear to be higher than the values obtained by Li and Armor [16] using Co-MFI. Promotion of Fe-MFI with 0.01 wt% Pt is sufficient for complete oxidation of the side-product carbon monoxide to CO_2.

Acknowledgement

The authors gratefully acknowledge financial support by Deutsche Bundesstiftung Umwelt.

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